

RATE EFFECT ON LITHIUM-ION GRAPHITE ELECTRODE PERFORMANCE

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Abstract

The electrochemical performance of lithium-ion graphite anodes with particle diameter in the range of 6-44 μm were evaluated at different charge/discharge rate (C/2 to C/60). The electrode capacity depends on both particle size and rate. The effect of rate on reversible capacity was least pronounced in anodes containing the smallest particles (6 μm). The electrochemical behavior is related to graphite's physical and chemical properties.

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Introduction

Lithium intercalation/de-intercalation processes in many carbonaceous materials are reversible processes. Under equilibrium conditions (i.e., as indicated by the presence of staged phases in graphitic carbon, the carbon capacity approaches 372 mAh/g, corresponding to theoretical value of one mole of lithium for every six mole of carbons (LiC_6). The carbon capacity is a function of the charge/discharge rate. At a given rate, the electrode performance may also depend on the carbon particle size (1, 2). While the effect of rate on capacity have been known, the rate effect on capacity of electrodes containing particles of various sizes have not been investigated. The goal of this work is to study the effect of rate on the performance (capacity, capacity loss) of lithium-ion anodes containing graphite particles of various sizes. The results are correlated with the graphite physical and chemical properties.

Experimental

Electrochemical studies were performed using a 64-channel Maccor battery tester. The experiments were carried out in a 15 ml, three-electrode cylindrical cell in which the electrodes and separator were positioned horizontally and stacked vertically. The geometric surface area of the working electrode was 1.12 cm². Lithium foils (Cyprus Foote Mineral) were used as the counter and reference electrodes. Whatman fiberglass filters (934-AH) were used as separators between the working and counter electrodes. The electrolyte was 0.5 M lithium trifluoromethanesulfonimide, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, (tradename HQ115, 3M Corp) in a 50:50 mixture of ethylene carbonate and dimethyl

carbonate (Grant Chemical). The cells were constructed and tested at $16 \pm 2^\circ\text{C}$ in a dry argon-atmosphere glove box (< 10 ppm water).

The experiments were studied using Lonza synthetic graphites with various sizes ranging from $6\text{ }\mu\text{m}$ to $44\text{ }\mu\text{m}$ in diameter. Superior natural flake graphites of similar particle dimensions but different L_c were also evaluated for comparison. The electrode preparation procedure has been described earlier (3). Each charge/discharge cycle consisted of constant-current steps at varying rate between C/2 to C/60 (based on LiC_6 composition) to a cut-off voltage at 0.005V (Li^+/Li) during discharge and at 1.5V during charge. Additional experiments were also performed with SFG6 (Lonza, $6\text{ }\mu\text{m}$) in which each cycle contained additional constant-voltage holds (for 4 hours) at 0.005V and 1.5V to assure complete lithium intercalation/deintercalation.

Results & Discussion

The charge/discharge profiles of SFG6 at various rate from C/2 to C/60 are shown in Figure 1a and 1b. SFG6 has particle size of $6\text{ }\mu\text{m}$ and L_c of $> 100\text{ nm}$ (as provided by the manufacturer). Electrode polarized significantly in experiments with fast rates (Figure 1a). For example, at C/2 rate, the electrode potential reached the lower voltage limit of 5 mV in 90 minutes in the first cycle. In the fourth cycle when formation of the passivating layer was completed, the lower limit was reached in only 25 minutes indicating significant overpotentials. The characteristic (i.e., equilibrium) constant-voltage plateaus associated with lithium staging in the graphite structure were not apparent until C/24 rate or at a slower rate as seen in Figure 1b.

The electrode capacity as a function of both rate and particle size is shown in Figure 2. At fast rates (C/2), the capacity of anodes with large particles ($44\text{ }\mu\text{m}$) was only 25% of that obtained under equilibrium conditions (C/24). The effect of rate on reversible capacity was less pronounced in anodes containing the smallest particles as seen in the figure. The reversible capacity of SFG6 achieved with C/24 rate (372 mAh/g) decreases by only 20% to 295 mAh/g at C/2. Initial data indicated that the irreversible capacity loss associated with the formation of the passivated layer did not depend on the rate.

Experiments with SFG6 at varying rates that included additional 4-hour constant-voltage holds during discharge (at 5 mV) and charge (at 1.5 V) were also carried out. Under these types of charge/discharge procedures, electrode capacity did not depend on the rate. Capacities at various rates approached $350\text{--}370\text{ mAh/g}$ even though the charge/discharge curves differed significantly due to large overpotentials at fast rates.

Constant-voltage discharge at 0.005V apparently facilitate lithium intercalation. It is expected that this type of discharge procedure would help to maximize intercalation kinetics.

Acknowledgment

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References

1. J.M. Tarascon and D.G. Guyomard, Extended Abstracts, Volume 93-1, Spring Meeting of the Electrochemical Society, Honolulu, HI, p. 102, May 16-21, 1993.
2. E Peled, D. Bar-Tow, A. Melman, E. Gorenrot, and Y. Lavi, Extended Abstract, Vol. 93-2, Fall Meeting of the Electrochemical Society, New Orleans, LA, p. 49, October 10-15, 1993.
3. T. D. Tran, J. H. Feikert, S. T. Mayer, X. Song and K. Kinoshita. Ab. No. 88, Fall Meeting of the Electrochemical Society, Miami Beach, FL, October 9-14, 1994.

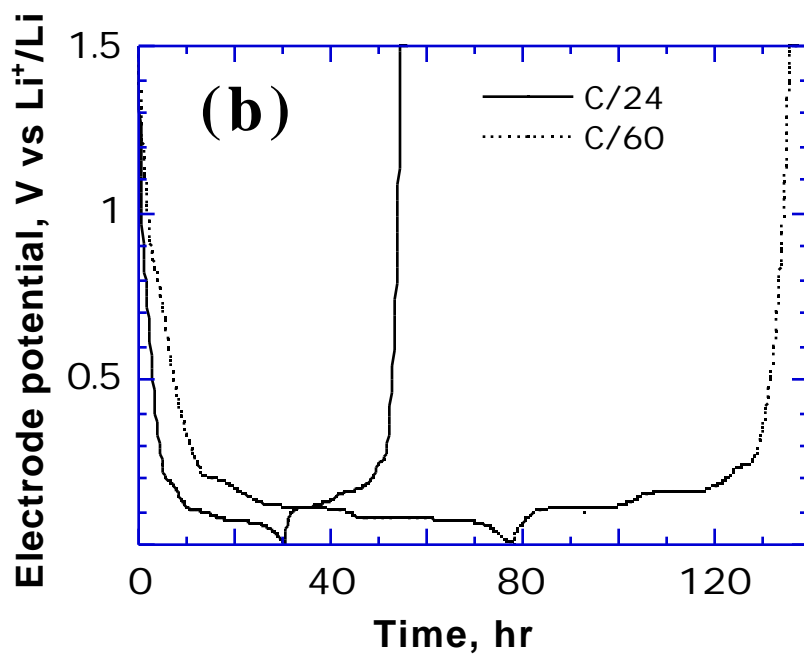
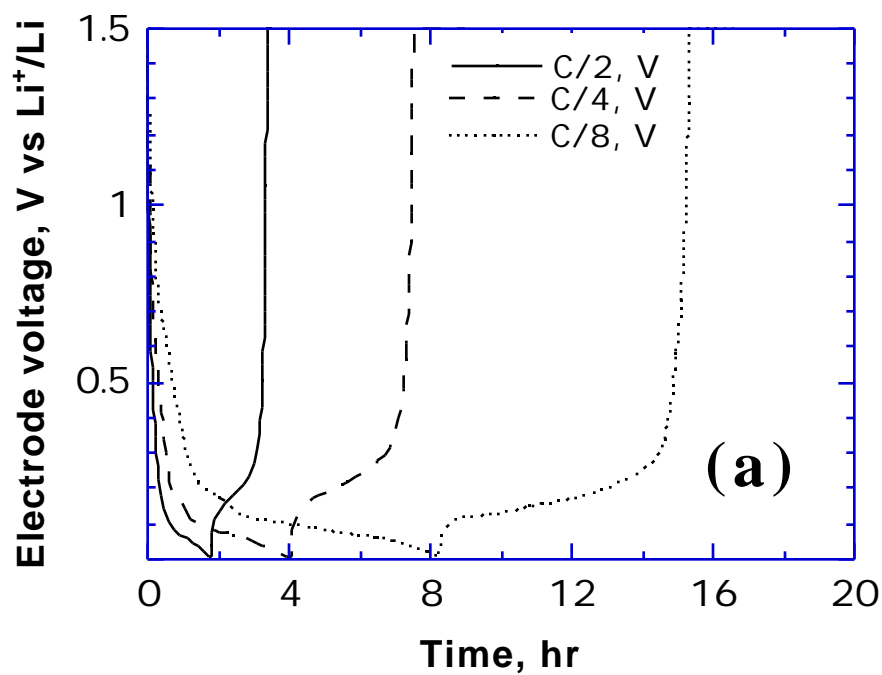


Figure 1. Potential profiles of Lonza SFG6 graphites in 0.5 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ / 50:50 EC-DMC with (a) C/2, C/4 and C/8 rate and (b) C/24 and C/60 rate.

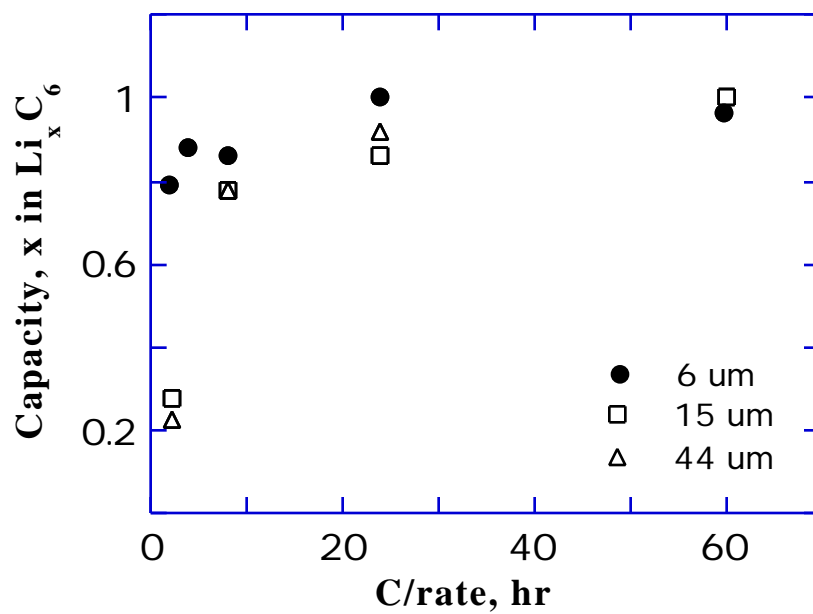


Figure 2. Reversible capacity (x in $\text{Li}_x \text{C}_6$) as a function of charge/discharge rate and particle size. First cycle data.